



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

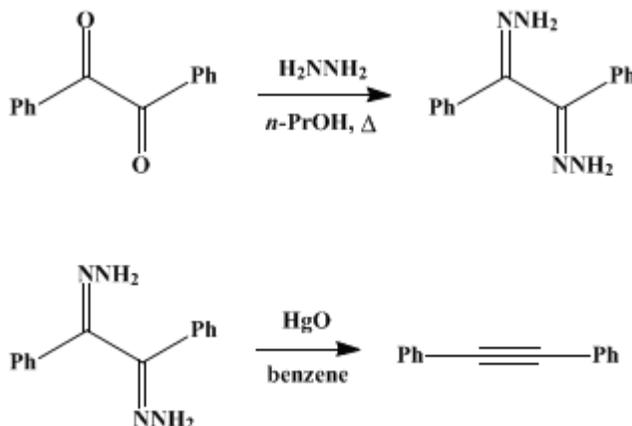
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.377 (1963); Vol. 34, p.42 (1954).

DIPHENYLACETYLENE

[Acetylene, diphenyl-]



Submitted by Arthur C. Cope, Douglas S. Smith, and Robert J. Cotter¹.
Checked by Charles C. Price and Thomas F. McKeon, Jr..

1. Procedure

A solution of 105.1 g. (0.5 mole) of **benzil** (Note 1) in 325 ml. of *n*-propyl alcohol is prepared in a 1-l. round-bottomed flask which is fitted with an efficient reflux condenser. To this solution 76 g. (1.30 moles) of 85% **hydrazine hydrate** (Note 2) is added, and the mixture (Note 2) is heated under reflux for 60 hours. The solution is cooled with an ice bath, and the **benzil dihydrazone** is separated by suction filtration. The crystals are washed with 200 ml. of cold, absolute **ethanol** and dried (Note 3) on the suction filter for 1 hour. The yield of **benzil dihydrazone** is 99–106 g. (83–89%), m.p. 150–151.5°.

The **benzil dihydrazone** is added to 480 ml. of reagent grade **benzene** in a 1-l. three-necked flask fitted with a reflux condenser and a sealed stirrer. A small amount of yellow **mercuric oxide** (2–4 g.) is added to the mixture with stirring to keep the **benzil dihydrazone** suspended, and the mixture is warmed slightly on a steam bath. **Nitrogen** is evolved, and the mixture turns gray. Additional yellow **mercuric oxide** is then introduced in small portions so as to keep the reaction mixture gently refluxing until a total of 240 g. (1.11 moles) has been added. The mixture is stirred for 1 hour and allowed to stand overnight. It is then filtered, and the residue (**mercury** and **mercuric oxide**) is washed with 100 ml. of **benzene**, which is combined with the original red **benzene** is filtrate. After drying over anhydrous **sodium sulfate**, the **benzene** is removed by distillation under reduced pressure by heating with a water bath. The residue is distilled from a flask connected to a short distillation head at 95–105°/0.2–0.3 mm. and yields 60–65 g. (67–73% from **benzil**) of **diphenylacetylene**, m.p. 59–60°. The product can be recrystallized from 100 ml. of 95% **ethanol**, m.p. 60–61° (Note 4).

2. Notes

1. Eastman Kodak Company white label grade **benzil** or material prepared by the procedure described in *Organic Syntheses*² is satisfactory.
2. **Hydrazine hydrate** (85%) as supplied by the Edwal Laboratories was used. On addition of this reagent to the **benzil** solution, the monohydrazone of benzil precipitates, but it redissolves readily on heating.
3. **Benzil dihydrazone** should not be dried in a vacuum desiccator, for it sublimes easily.
4. **Diphenylacetylene** prepared by this method has the advantage of being uncontaminated with **stilbene**, with which it forms a solid solution not readily separable.³ **Di-*p*-tolylacetylene**⁴ and α -naphthylphenylacetylene⁵ have been prepared by the same method in high yields.

3. Discussion

In addition to the methods mentioned in a previous preparation,⁶ diphenylacetylene has been prepared by the action of potassium hydroxide on 5,5-diphenyl-3-nitroso-2-oxazolidone (100%),⁷ on meso-stilbene dibromide in triethylene glycol,⁸ and on stilbene tetrabromide in butyl alcohol,⁹ by the condensation of bromobenzene with sodium phenylacetylde in liquid ammonia,¹⁰ by the oxidation of benzil dihydrazone with silver trifluoroacetate in triethylamine,¹¹ and by the pyrolysis of α -benzoylbenzylidenetriphenylphosphorane.¹² The present procedure is a modification of that of Schlenk and Bergmann.¹³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 531](#)

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. [Org. Syntheses Coll. Vol. 1, 87 \(1941\)](#).
3. Pascal and Normand, *Bull. soc. chim. France*, [4] **13**, 151 (1913).
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7. Newman and Kutner, *J. Am. Chem. Soc.*, **73**, 4199 (1951).
8. Fieser, *J. Chem. Educ.*, **31**, 291 (1954).
9. Drefahl and Plötner, *Chem. Ber.*, **91**, 1280 (1958).
10. Scardiglia and Roberts, *Tetrahedron*, **3**, 197 (1958).
11. Newman and Reid, *J. Org. Chem.*, **23**, 665 (1958).
12. Trippett and Walker, *J. Chem. Soc.*, **1959**, 3874.
13. Schlenk and Bergmann, *Ann.*, **463**, 76 (1928).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

monohydrazone of benzil

α -naphthylphenlacetylene

[ethanol](#) (64-17-5)

[ammonia](#) (7664-41-7)

[Benzene](#) (71-43-2)

[sodium sulfate](#) (7757-82-6)

[nitrogen](#) (7727-37-9)

[mercury](#) (7439-97-6)

mercuric oxide (21908-53-2)
butyl alcohol (71-36-3)
Benzil (134-81-6)
potassium hydroxide (1310-58-3)
bromobenzene (108-86-1)
n-propyl alcohol (71-23-8)
hydrazine hydrate (7803-57-8)
sodium phenylacetylide
stilbene
Diphenylacetylene,
Acetylene, diphenyl- (501-65-5)
triethylamine (121-44-8)
Benzil dihydrazone (4702-78-7)
5,5-diphenyl-3-nitroso-2-oxazolidone
triethylene glycol (112-27-6)
stilbene tetrabromide
silver trifluoroacetate
 α -benzoylbenzylidenetriphenylphosphorane
Di-p-tolylacetylene
meso-stilbene dibromide